

① Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H NMR = proton NMR
 ^{13}C NMR = carbon NMR

NMR-active atoms have a nuclear spin (I) $\neq 0$.

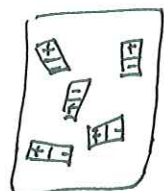
For us, $I = 1/2$ nuclei are most important
 ^1H , ^{13}C , ^{15}N , ^{19}F , ^{29}Si

end of Thurs.

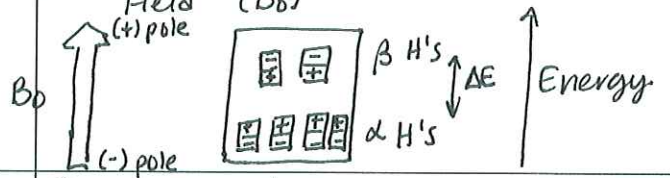
② Extremely Basic Principle: ^1H NMR

① Spinning Charged Particle generates a magnetic field.

② Think of our proton as a "bar magnet."

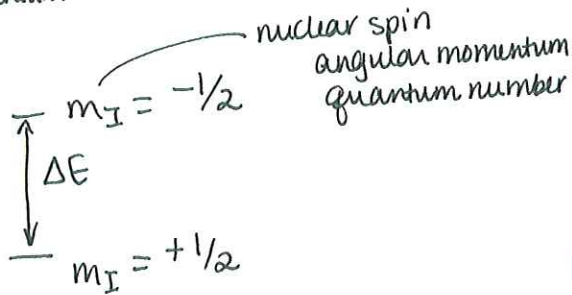
③  flask full of bar magnets in random orientations.

④ Place in an external "Applied Magnetic Field" (B_0)

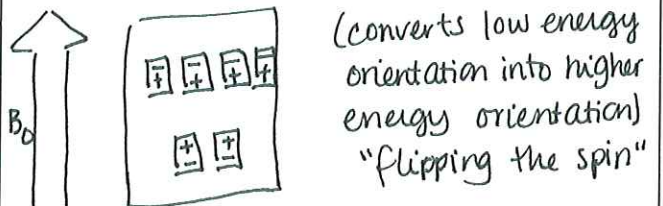


③ Some H's align against B_0 (Higher Energy)
 More align w/ B_0 (Lower Energy)

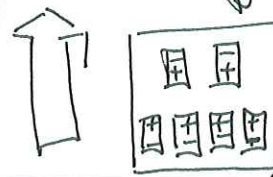
Quantum Mechanics "Spin States"



④ Add energy (radiowaves)



Relaxation
 heat



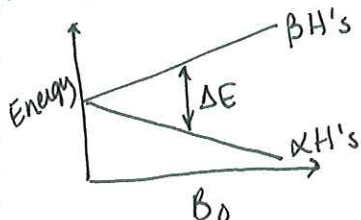
⑤ ΔE depends on
 $E = h\gamma B_0 / 2\pi$

B_0 = strength of applied field

γ = gyromagnetic ratio (characteristic of each nuclei)

h = Planck's constant

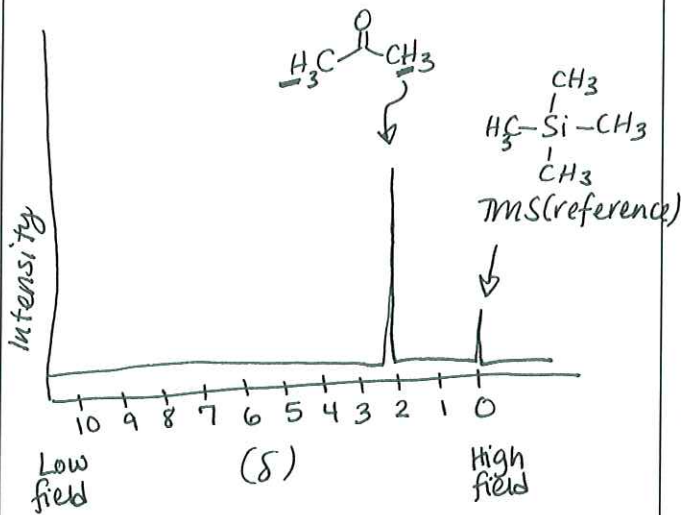
So: ΔE increases as B_0 increases.



⑥ NMR Spectrometer:

- Supplies B_0
- Source of radiowaves (to flip the spin)
- Detects the absorption of energy (resonance)

⑦ Resulting Plot (spectra):



⑧

δ = chemical shift
in ppm, parts per million of B_0
with respect to TMS

Chemical Shift: the resonance frequencies of each H of an organic molecule is strongly dependent on its local electronic environment.

∴ We see a signal for each "different" H in a molecule.

⑨

What makes a H "different"?

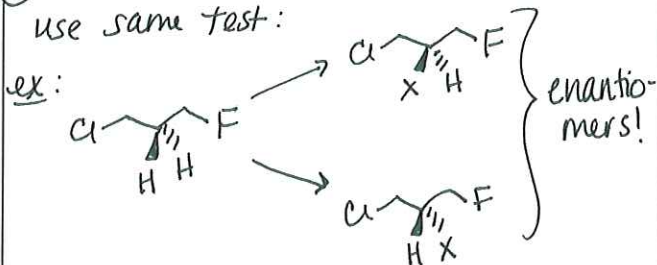
Classification of H's:

① Chemically Equivalent H's: 2 or more nuclei are said to be chemically equivalent when they have the same chemical shift.

② Magnetically Equivalent H's: 2 or more nuclei are said to be magnetically equivalent when both of the following conditions are met:
(a) The nuclei are chemically equivalent.
(b) All nuclei in the group have the same coupling constant to any/each other single nucleus in the molecule (more later).

② Enantiotopic H's

use same test:

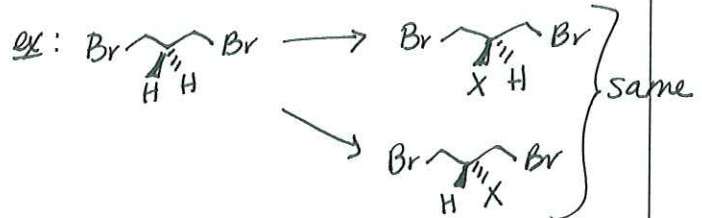


H's \Rightarrow enantiotopic \Rightarrow Chemically Equivalent (same chemical shift)

⑩ Stereochemical Classifications

① Homotopic H's = Chemically Equivalent

Test: Replace each H in question w/ an X. If resulting molecules are the same, then H's = homotopic

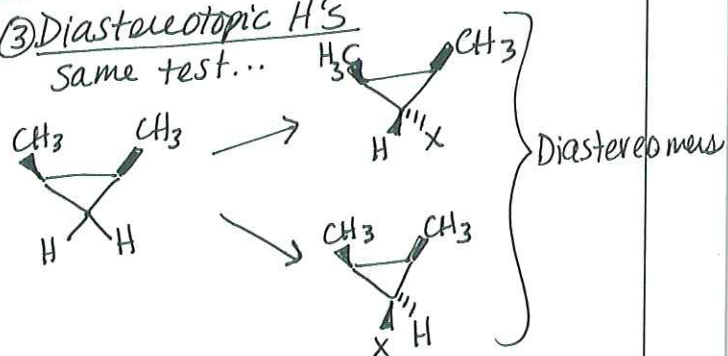


H's = homotopic \Rightarrow Chemically equivalent
 \Downarrow
Same chemical shift (ppm)

②

③ Diastereotopic H's

Same test...



H's = diastereotopic
 \Downarrow
Chemically non-equivalent
 \Downarrow
Distinct chemical shifts (different ppm)

18

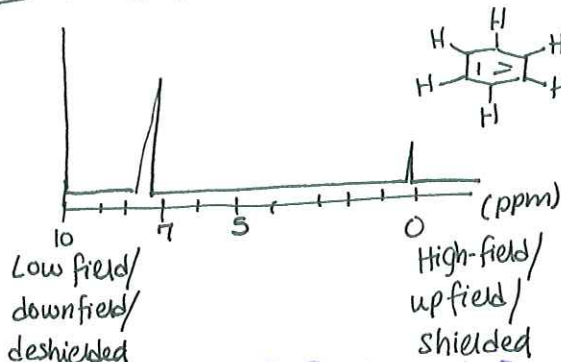
General Fxnal Group Resonances (Table 15.4)

Hydrogens in	Approximate δ (ppm)
$-\underline{\text{C}}\text{H}_3$	0.8-1.0
$\text{O}-\underline{\text{C}}\text{H}$	3.1-3.8
$\text{C}=\underline{\text{C}}\text{H}$ (alkene)	5.0
$\text{Ph}-\text{H}$	7-8
$\text{R}-\underline{\text{C}}\text{H}$	9-10
$\text{R}-\underline{\text{C}}\text{OH}$	10-13

19

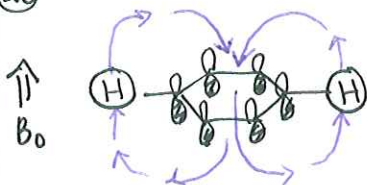
The more "deshielded" a H, the more downfield its δ .

ex: Aromatic H's resonate at low field



* Shielded by what? Electrons \Rightarrow B_i (induced magnetic field)

20



Applied magnetic field induces a circulation of e⁻s in the ring (ring current), which opposes B_0

Induced magnetic field (B_i)

What Hydrogen feels = $B_{net} = B_0 + B_i$

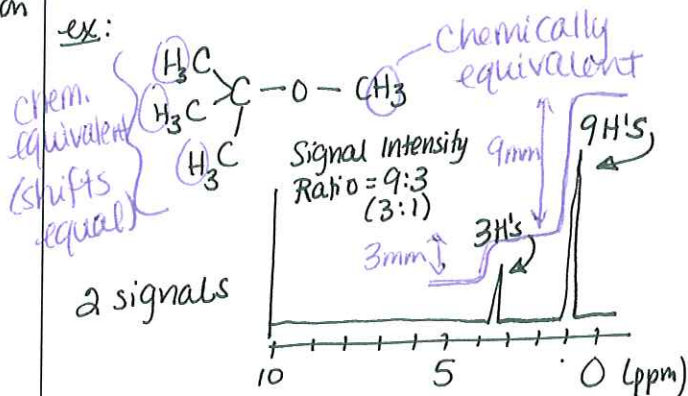
\therefore Requires lower applied field to resonate.

21

Integration

- Counts how many H's give rise to each signal (shift)
- Based on signal intensity

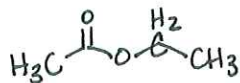
ex:



22

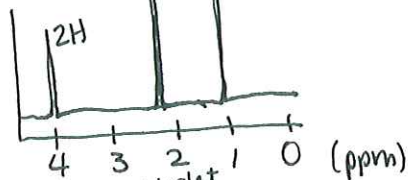
Coupling

Consider Ethyl Acetate

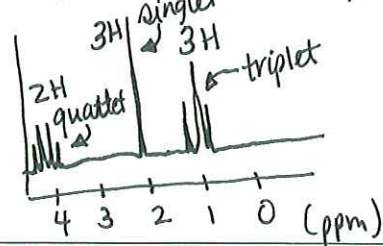


3 sets of chemically distinct H's

Expect:



Actual:

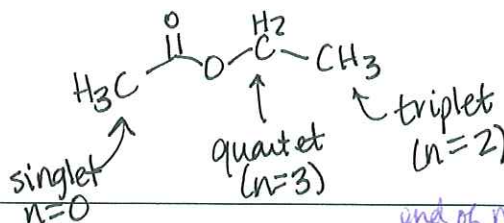


23

What's going on?

(N+1) neighbor Rule: Signal will be split into (n+1) peaks where n = # of "equally coupled" H's on a neighbouring C atom.
 \hookrightarrow most cases = magnetically equivalent.

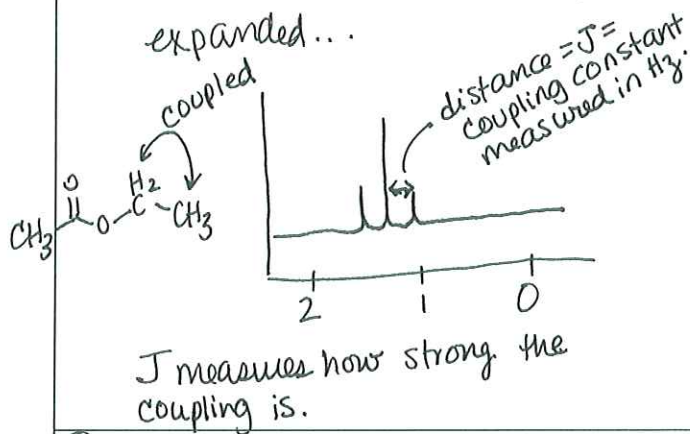
If spectra can be predicted by (n+1) rule \Rightarrow 1st order spectra (simple spectra).



end of Monday

24) Simplified explanation for (n+1) Rule:

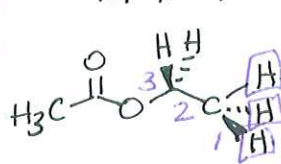
The spin states for one set of H's are magnetically coupled to the spin states of their neighboring H's → multiplets in the spectra.



25)

Magnetically Equivalent H's:

- Must be chemical shift equivalent (chemically equivalent)
- Must be coupled equally to each other single nucleus (measured in # of bonds)



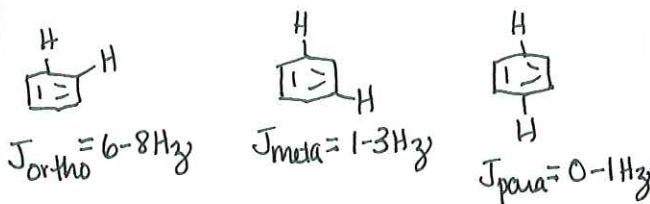
Are these H's magnetically equiv?

- Chemically equiv
- Couple equally to every other nuclei (3 bond coupling)

26)

Aromatic Coupling

Coupling b/w H's on aromatic rings can occur where one H may couple w/ another H farther away than its nearest neighbor.

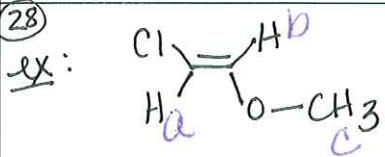


27)

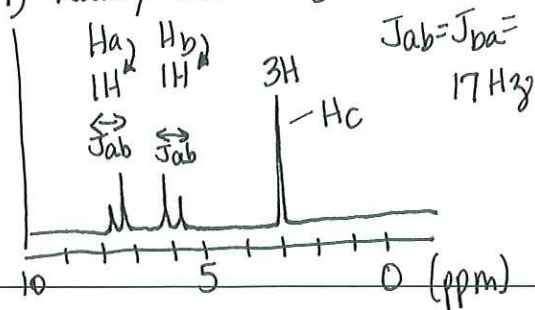
Interpreting Spectra: using (n+1) rule & tree diagrams.

- Identify & label chem. equiv H's (a, b, c...)
- Identify & label non-magnetically equiv H's (a', b', c')
- Use charts & integration values to predict region (ppm) of each set of H's
- Assign multiplicity using (n+1) rule / Tree Diagram.

28)

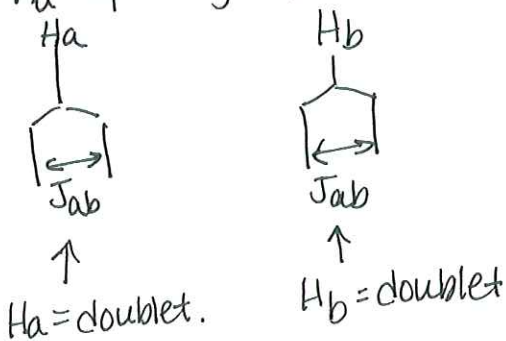


- H_a & $H_b \approx 5-7.5 \text{ ppm}$
 $H_c \approx 3-4 \text{ ppm}$
- (n+1) Rule / tree diagram.



29)

H_a split by H_b & vice versa



H_c : No neighboring H's (singlet)

end of Tues.

On Thurs: Correction: CH₂'s of EtOAc = enantiotopic.

30

Chem Equiv: H_a, H_b, H_c

if rapid rotation around C-CH₃, then H_a's = Chem. equiv.
H_b's = Chem. equiv.

ex: Cc1ccc(Br)cc1

H_a, H_a', H_b, H_b' ~ 7 ppm
H_c ~ 2 ppm

31

Tree Diagrams:

H_a, a' H_b, b' H_c

doublet 6.9 ppm doublet 7.2 ppm Singlet @ 2.2 ppm

Luckily J_{ab}' = 0
so spectra appears 1st order.

★ Examples in handouts. ★

32

NMR of alcohols & amines

Ⓞ: Ethanol → D = 2H = deuterium

CCO + D₂O → CC(=O)OD + H₂O

"exchange"

very pure EtOH n=2 (triplet)

Look @ H_b's:

8 lines (doublet of quartets)

quartet

NMR silent (no signal)

33

Under Normal Conditions

trace acidic or basic impurities + deuterium source (solvent)

OH + OD

equilibrating mixture

"average" NMR signal

→ not well resolved NMR peaks

34

Complicated Spectra (Deviation from (n+1) Rule)

- when H's are very magnetically different (different chem. shifts/ppm), we expect 1st order spectra → FOLLOW (n+1) RULE.
- when H's are slightly magnetically different → COMPLEX SPECTRA. Do not follow (n+1) rule exactly.

35

→ Δδ > 10 J_{ab}

The difference in chemical shift between 2 H's must be 10 times greater than their coupling constant.

On exams: only 1st order spectra. 😊

36 ^{13}C NMR

- ^{13}C has $I = 1/2$ (NMR active).
- Natural Abundance = 1.1%
(don't see effect of ^{13}C in ^1H NMR)
- No ^{13}C - ^{13}C coupling of adjacent C's
- Eliminate ^1H - ^{13}C coupling experimentally (broad band decoupling)

So each different carbon =
| chemical shift.

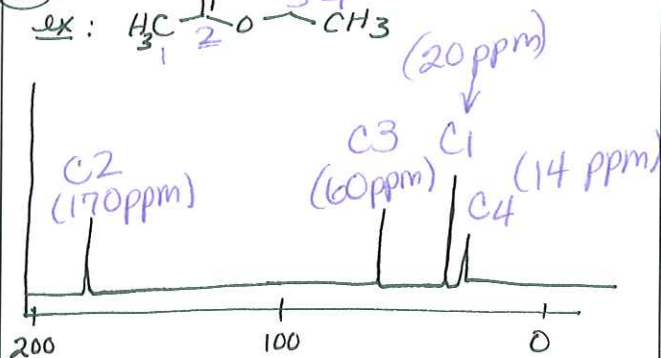
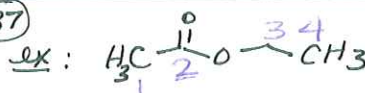
See Table 15.5 for resonances of
common C's.

38

Example(s) of Solving an
Unknown... (Handouts)

40

37



39

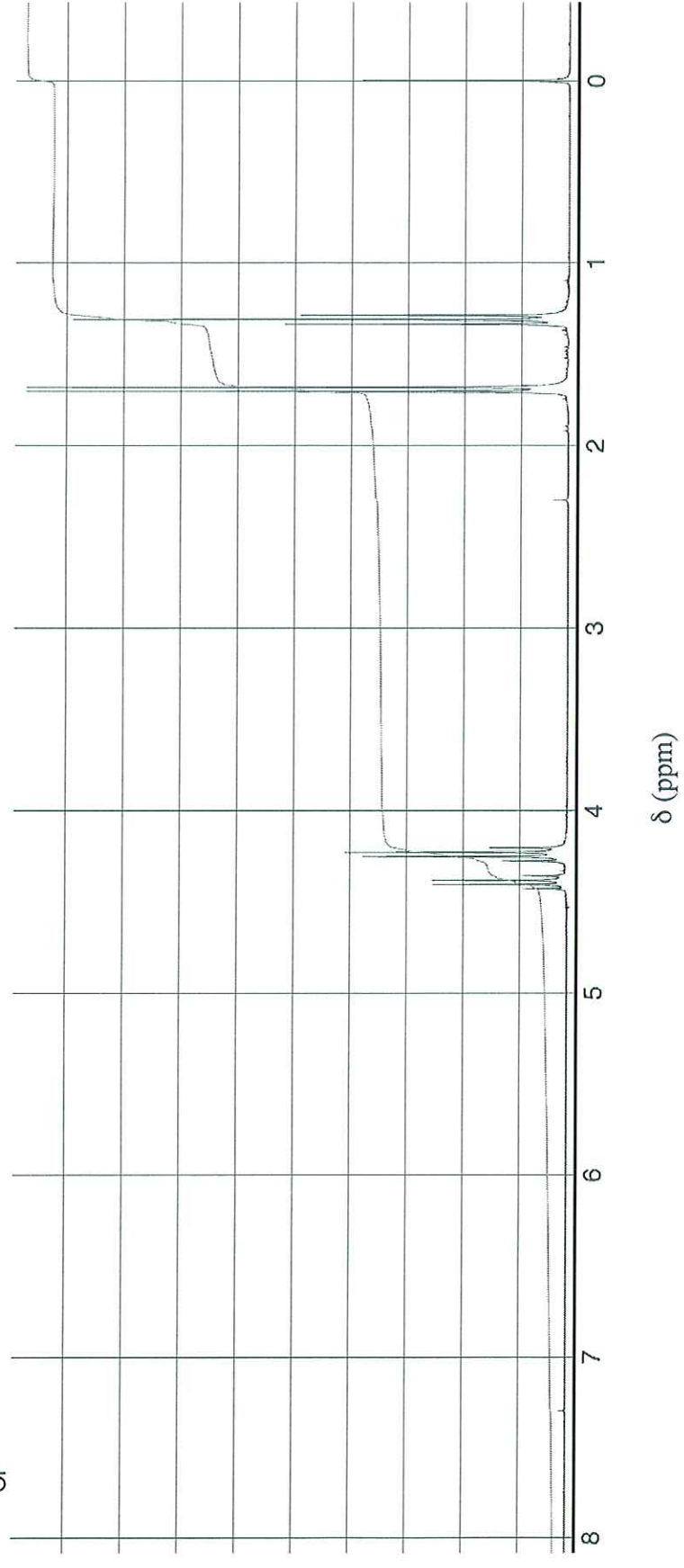
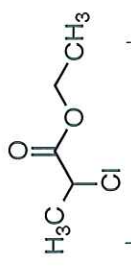
Thank you, Chem 322
Students! It has been
a pleasure to get to
know you & teach you
this semester!

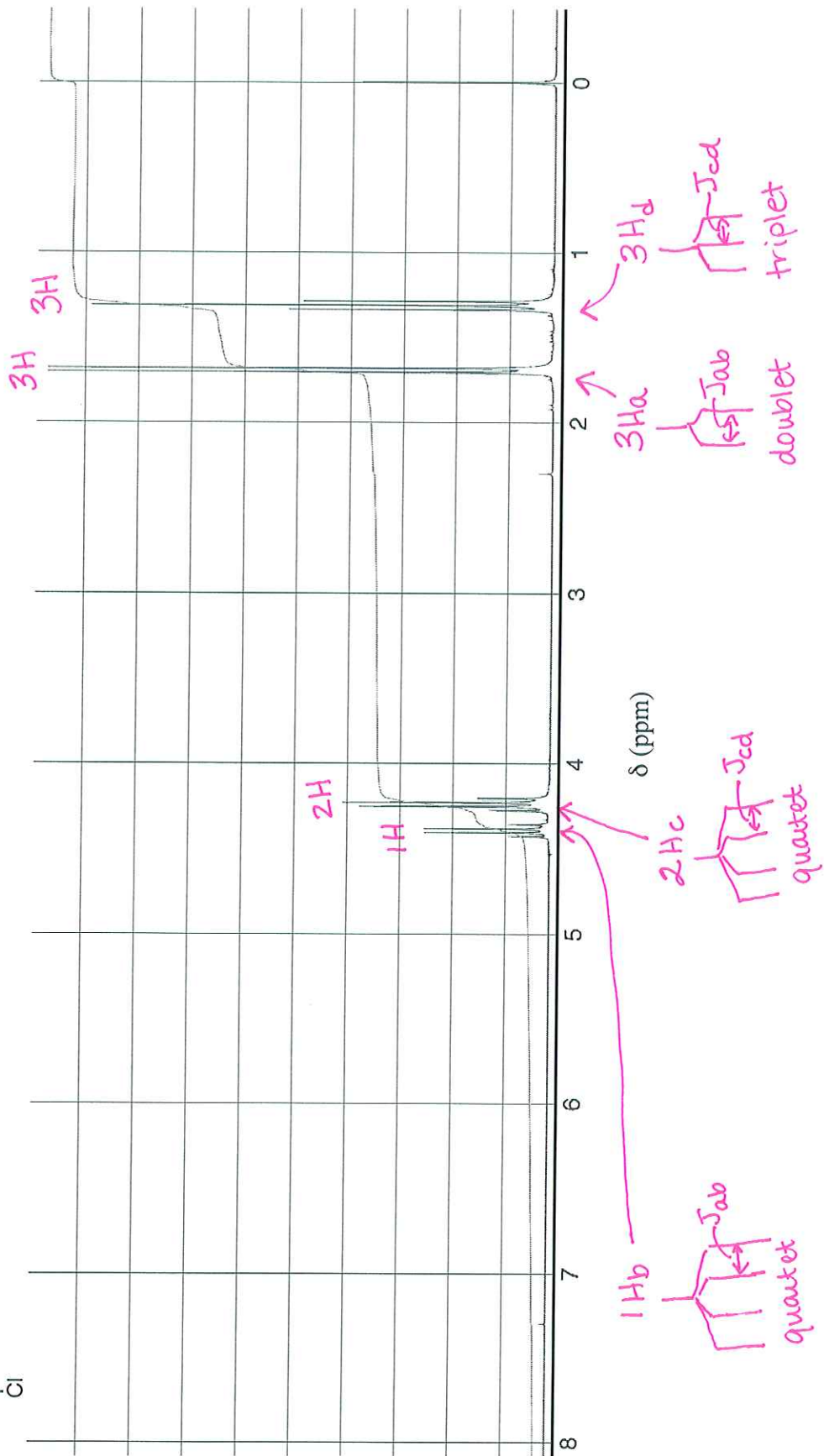
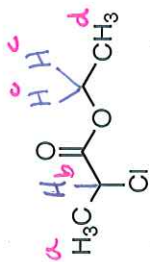
- Prof M.

(Prof Don Watson starts next
week.)

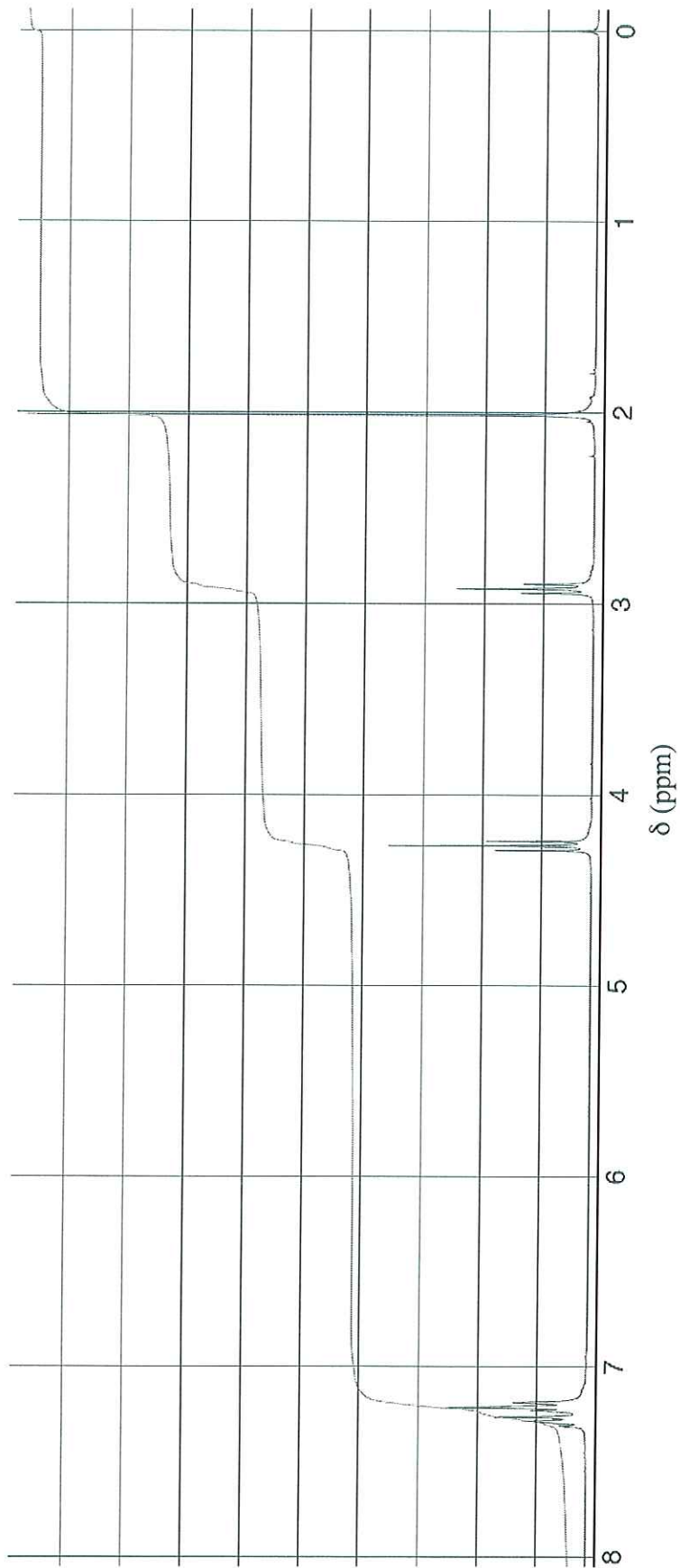
41

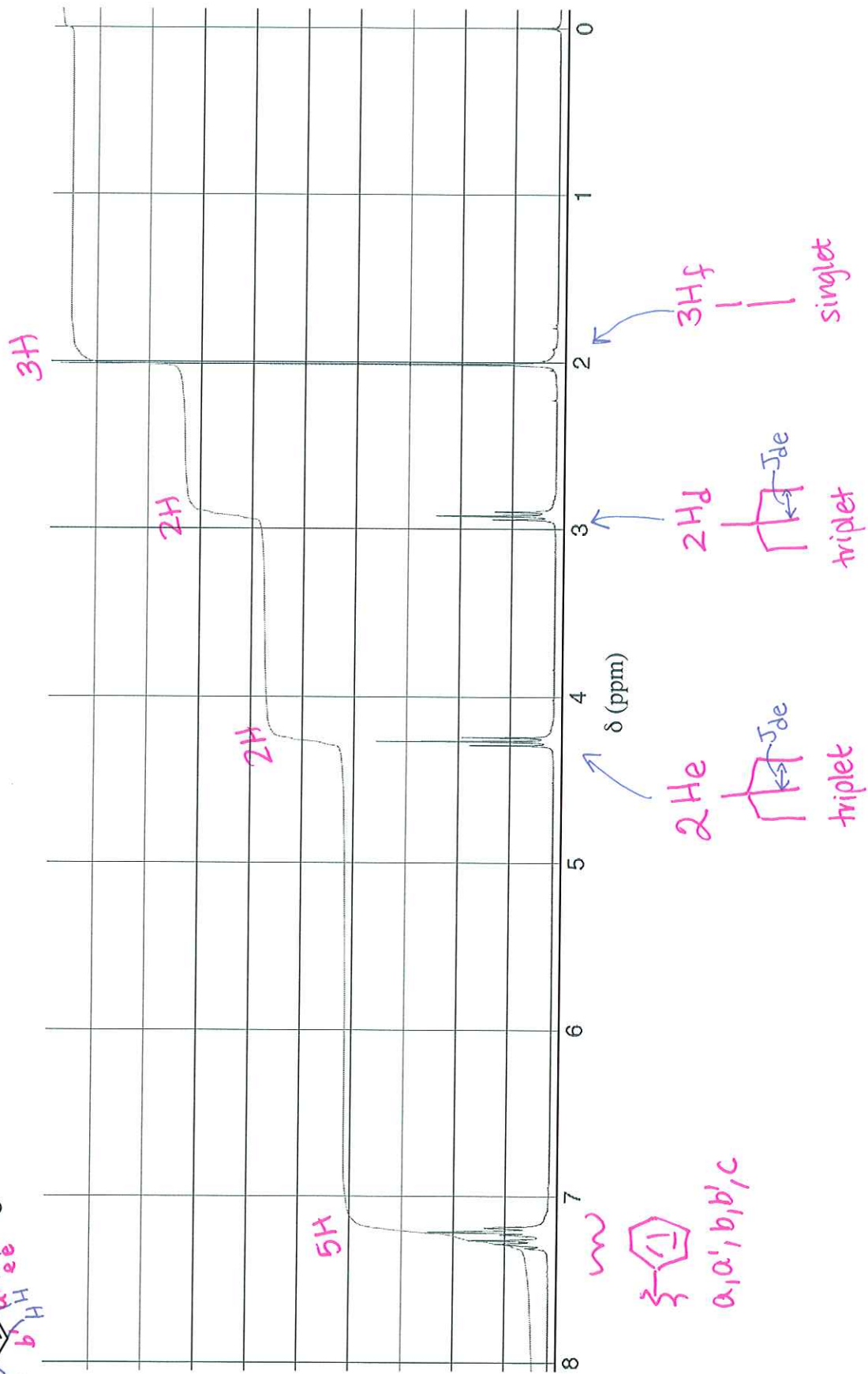
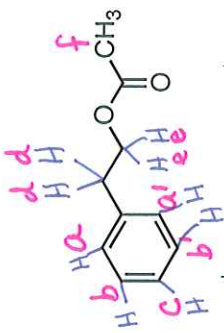
Assign the peaks for this compound (Answer on next page).



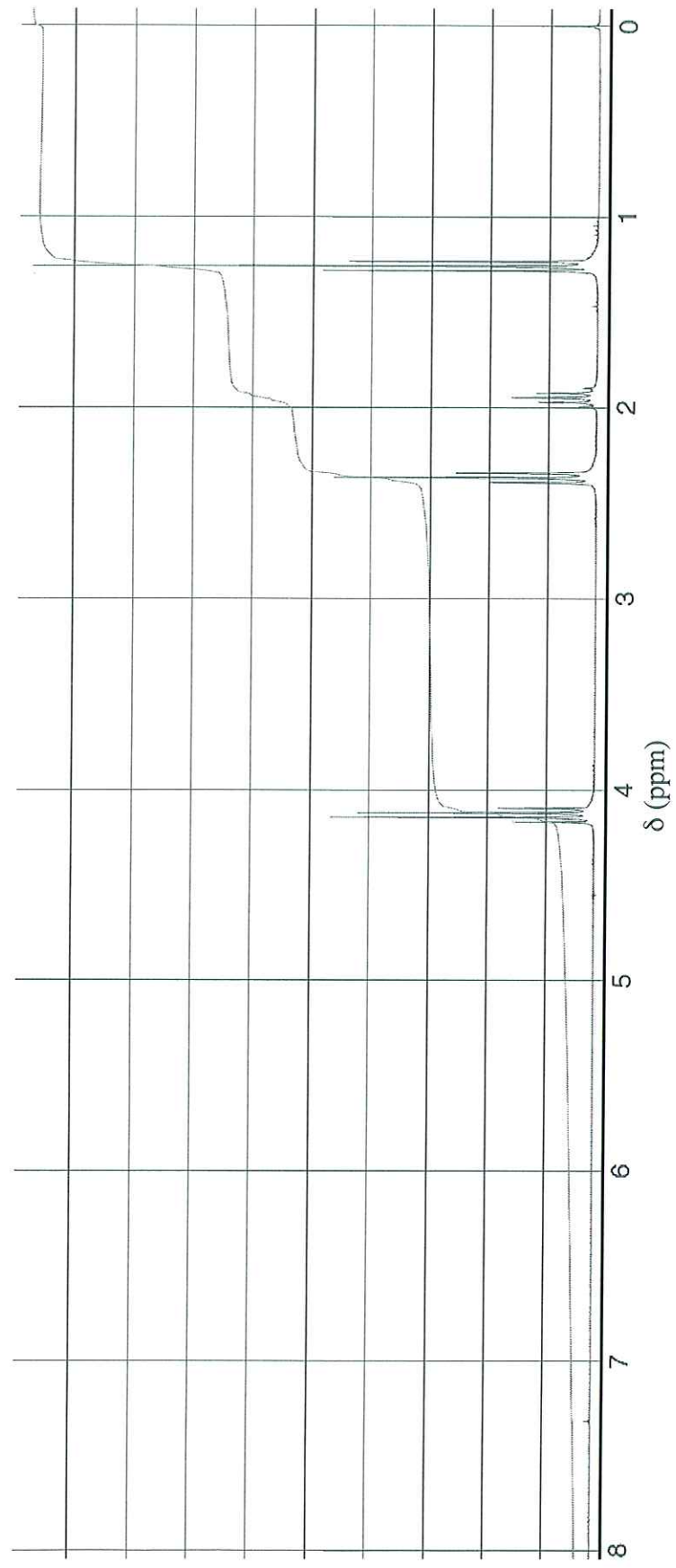


Assign peaks for this compound (answer on next page).

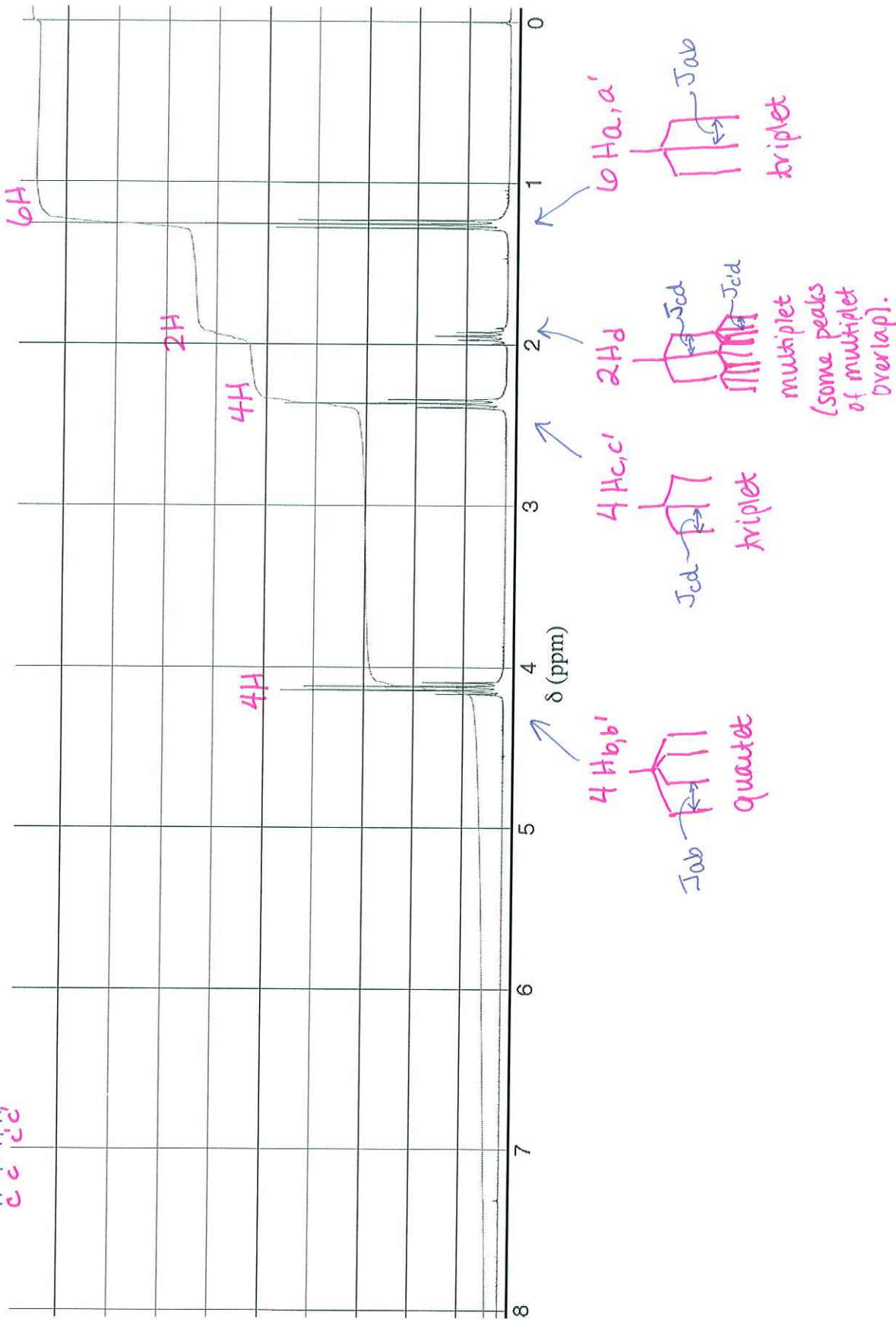
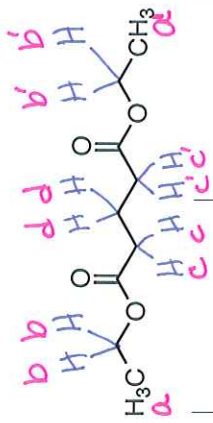


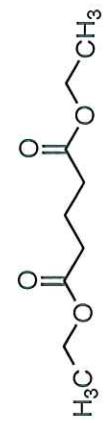


Assign peaks for this compound.

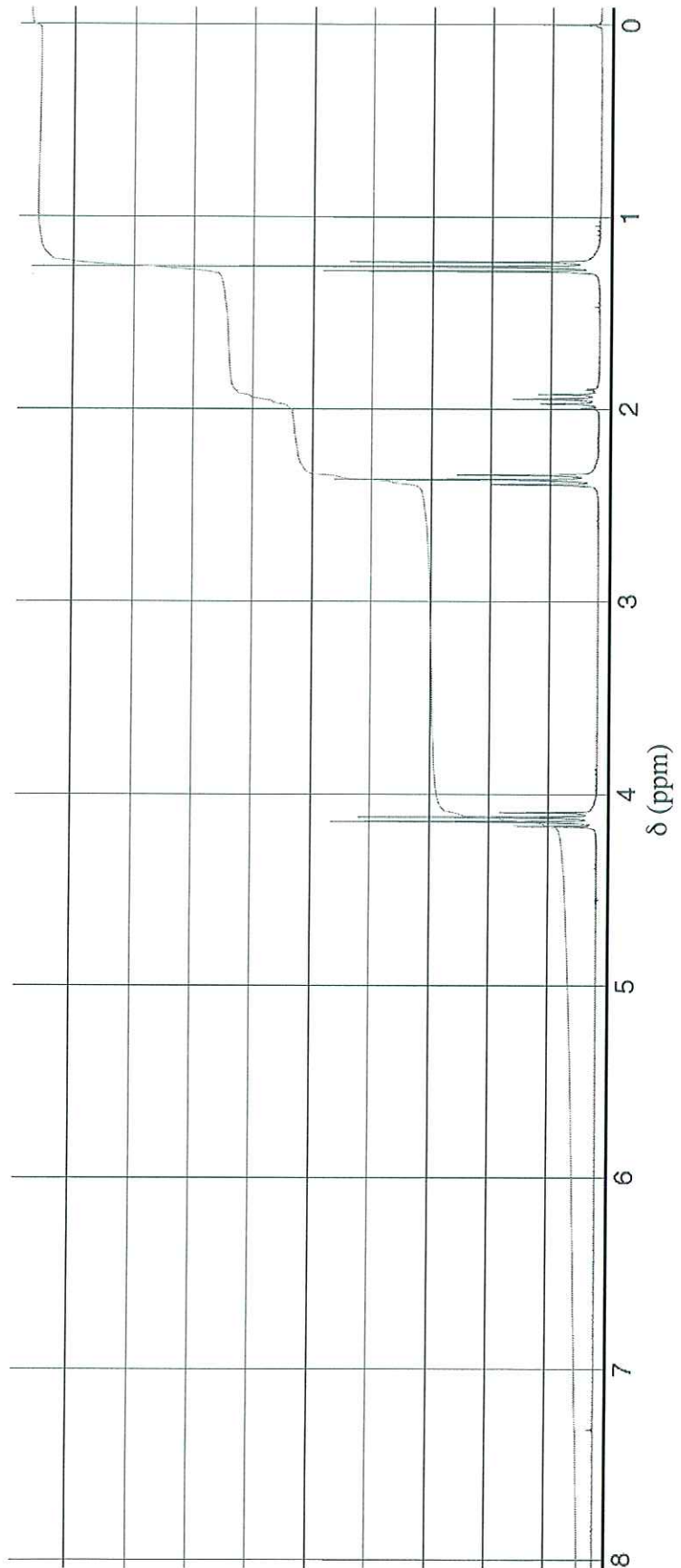


Peak ratio = 2:2:1:3 \Rightarrow 4:4:2:6

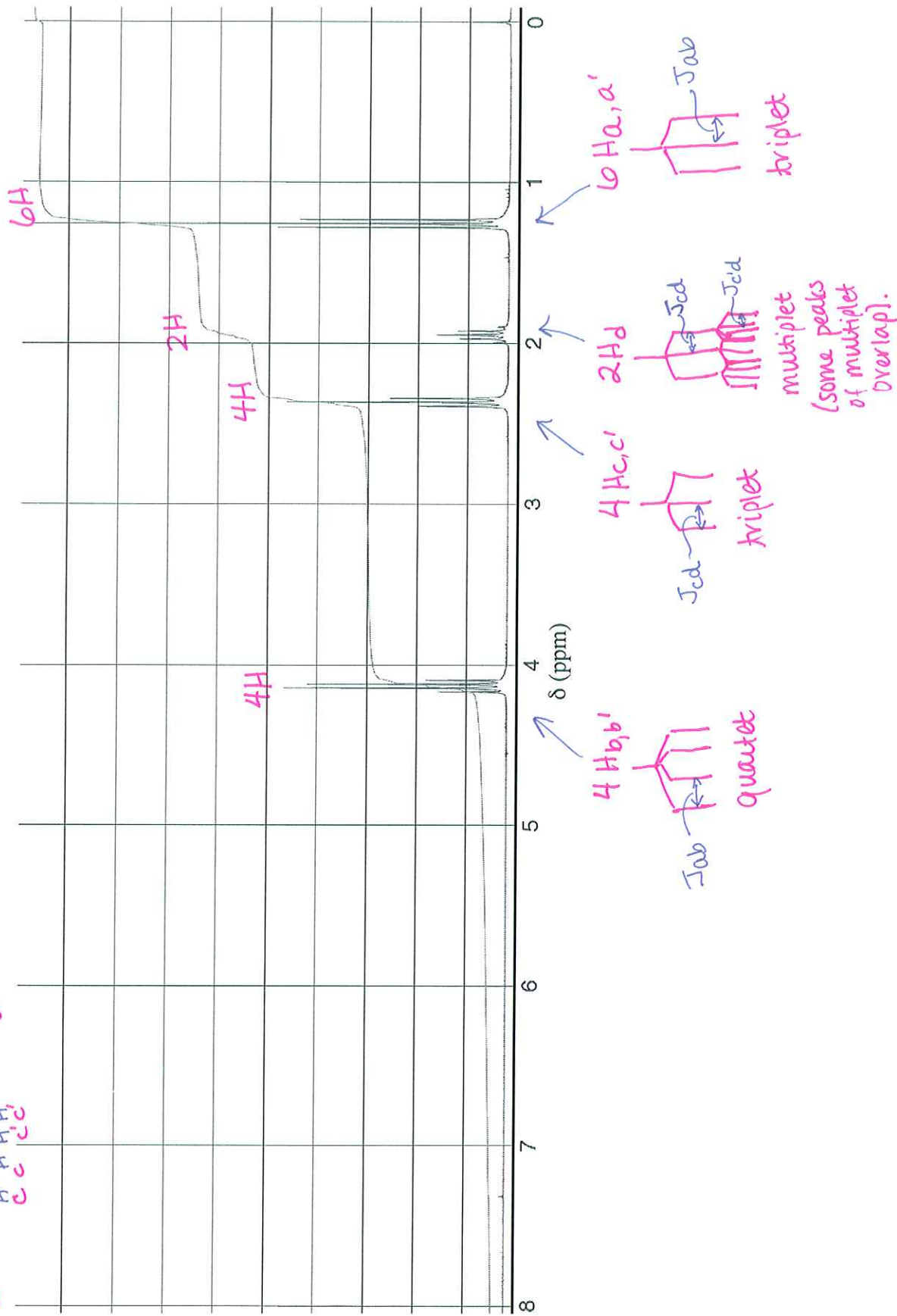
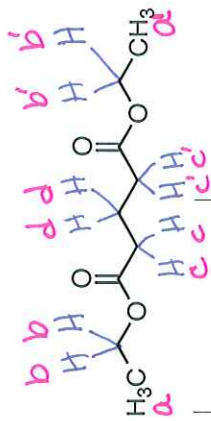




Assign peaks for this compound.



Peak ratio = 2:2:1:3 \Rightarrow 4:4:2:6



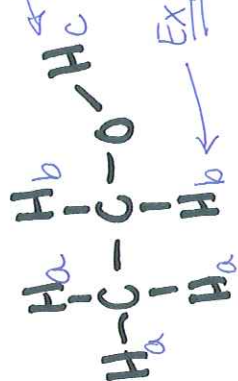
in CDCl₃

Expect H_c → triplet...

split by H_c

Expect H_b → doublet of triplets quartets

split by 3H_a



in CDCl₃

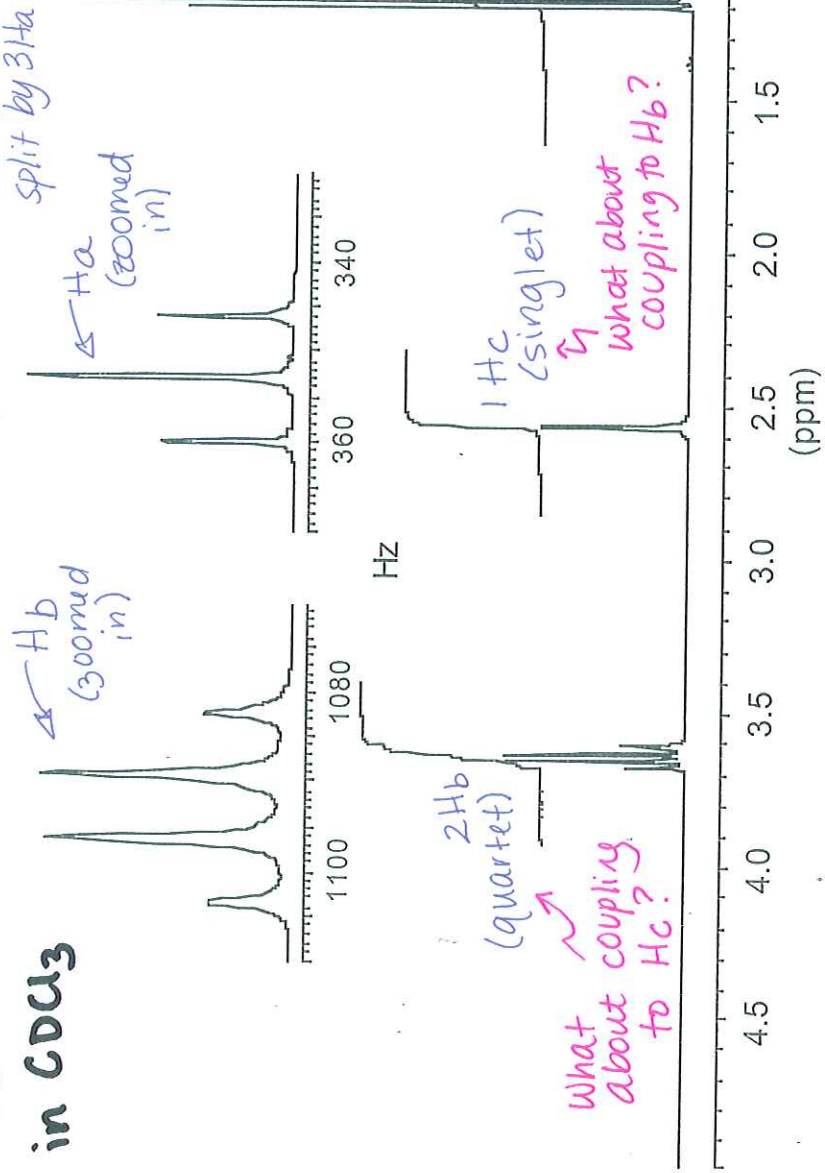


FIGURE 4.32. CH₃CH₂OH in CDCl₃ at 300 MHz, allowed to stand at room temperature overnight exposed to air. The CH₂ peaks are broadened by residual coupling to OH.

From R.M. Silverstein, F.X. Webster. *Spectrometric Identification of Organic Compounds*, 6th Edition.

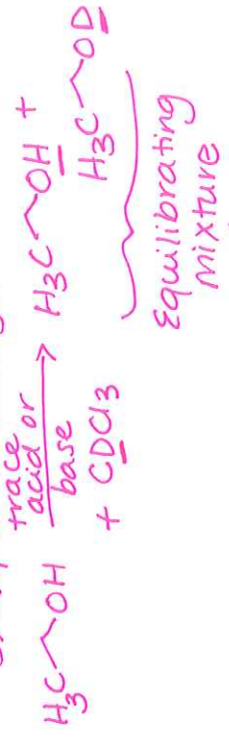
3H_a (triplet)

H's on Oxygen & Nitrogen are special:

1) O-H (or N-H) shift (ppm) depends on concentration, temperature & polarity of solvent!!

2) Hydrogen-bonding (solvent & molecule or molecule-molecule)

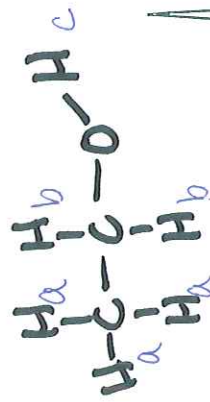
3) Rapid Exchange



Poorly resolved

NMR peaks. (not on the molecule long enough to affect -CH₂-).

If mostly H₃C-OH, you won't see the -OH peak.



in dry
DMSO-d₆

CH₃CH₂OH
in DMSO - d₆

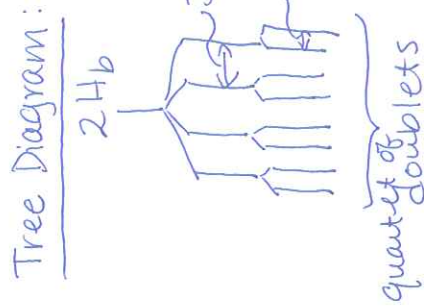
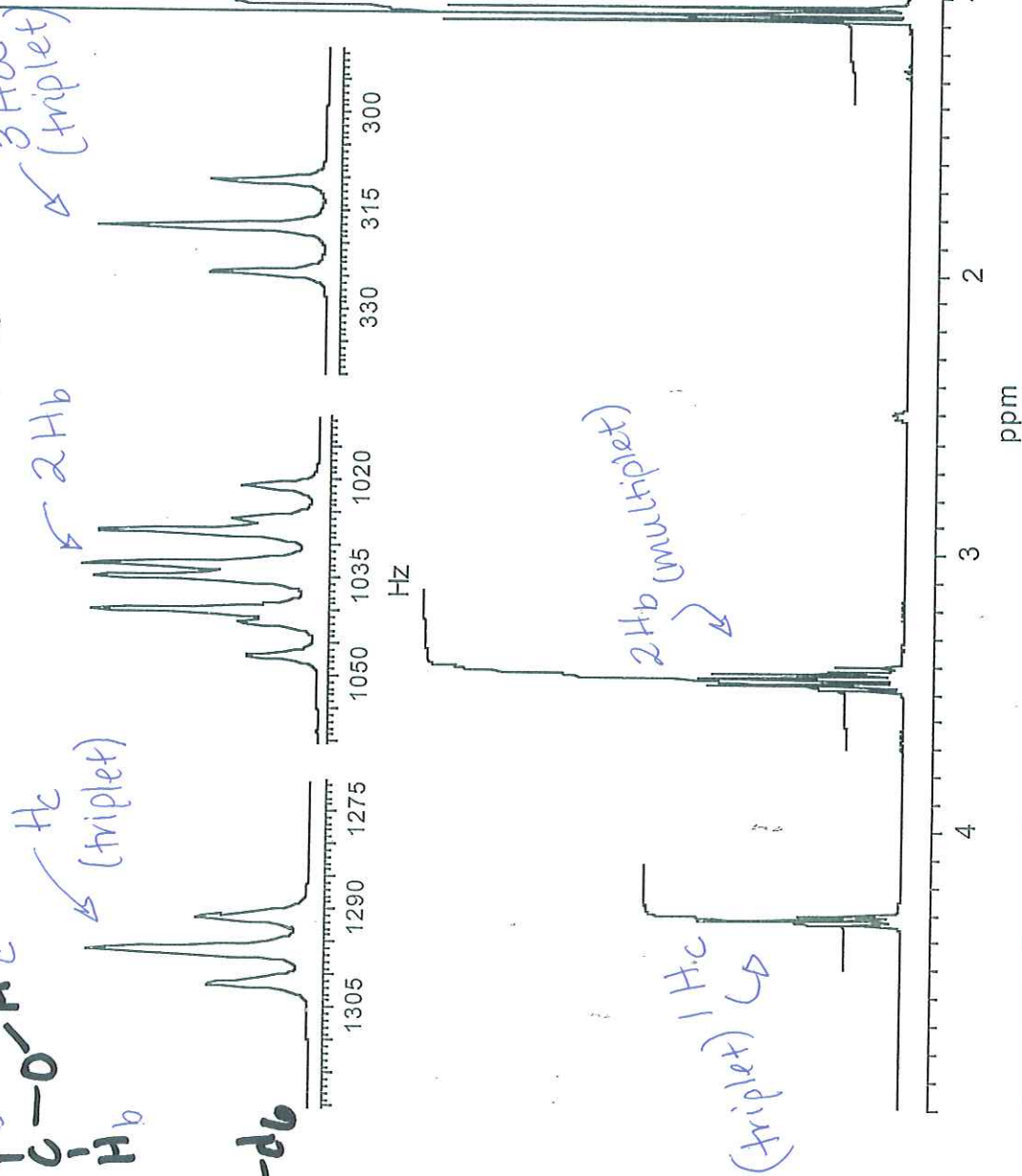


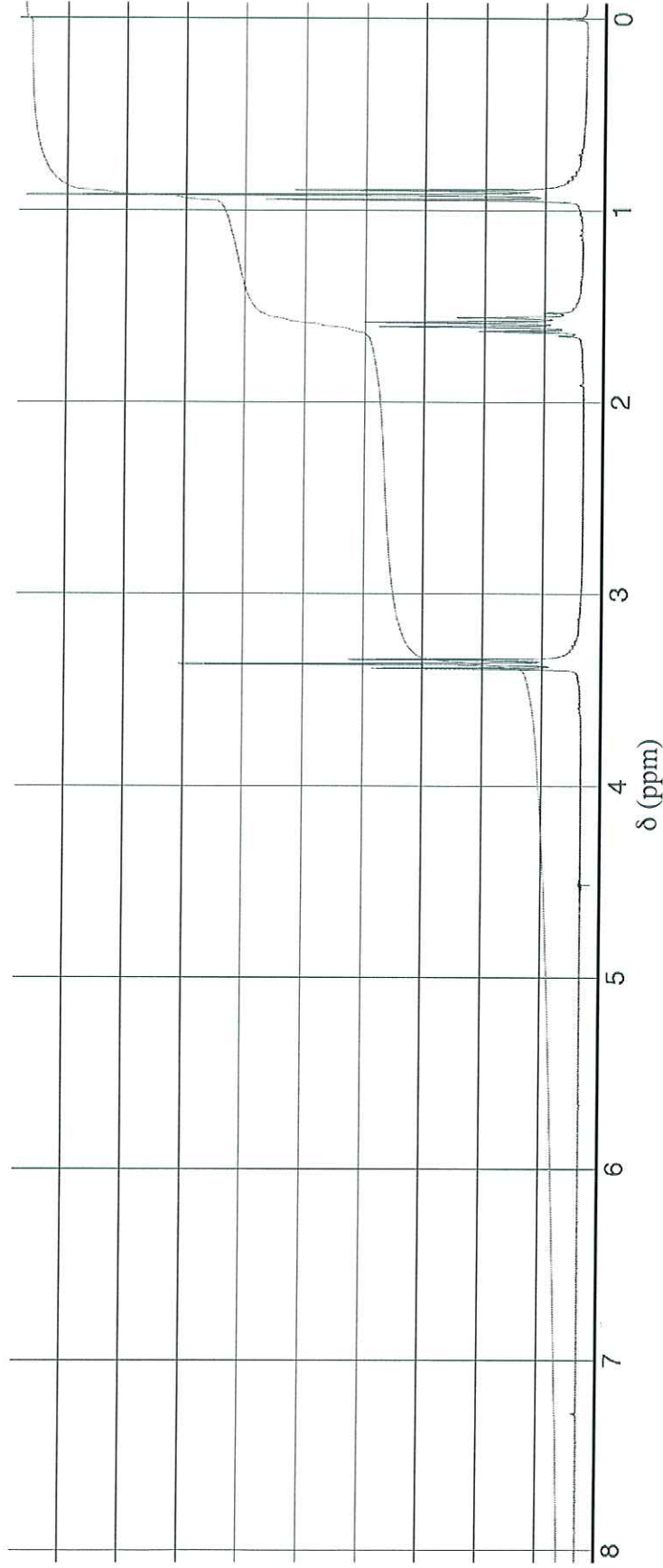
FIGURE 4.33. CH₃CH₂OH run in dry deuterated DMSO at 300 MHz.

From R.M. Silverstein, *Fa. Webster. Spectrometric Identification of Organic Compounds*, 6th Edition.

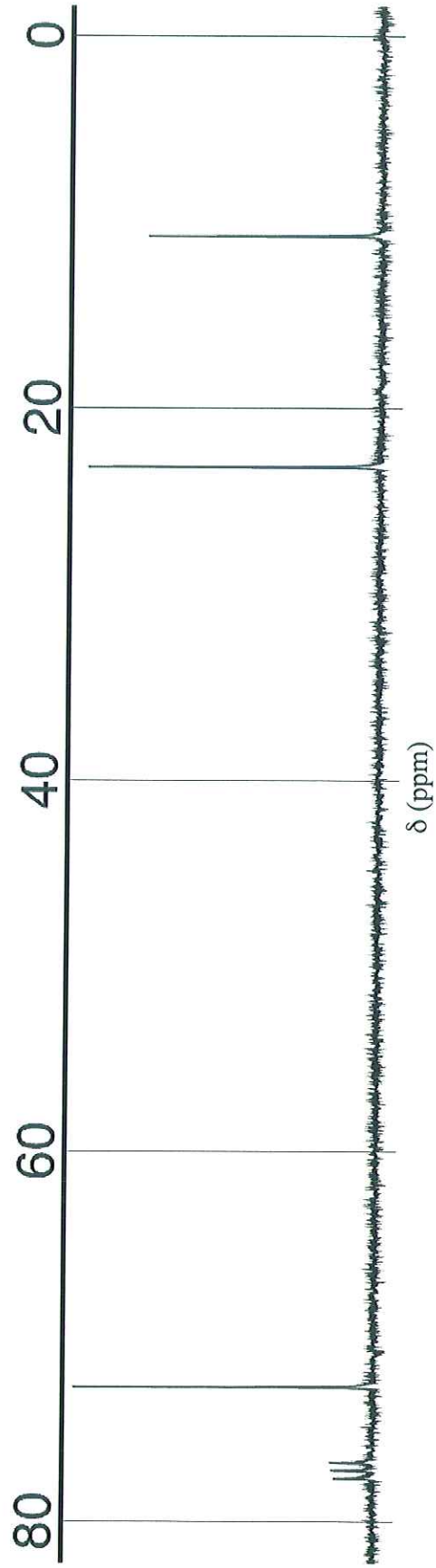
What is this compound?



1H
NMR

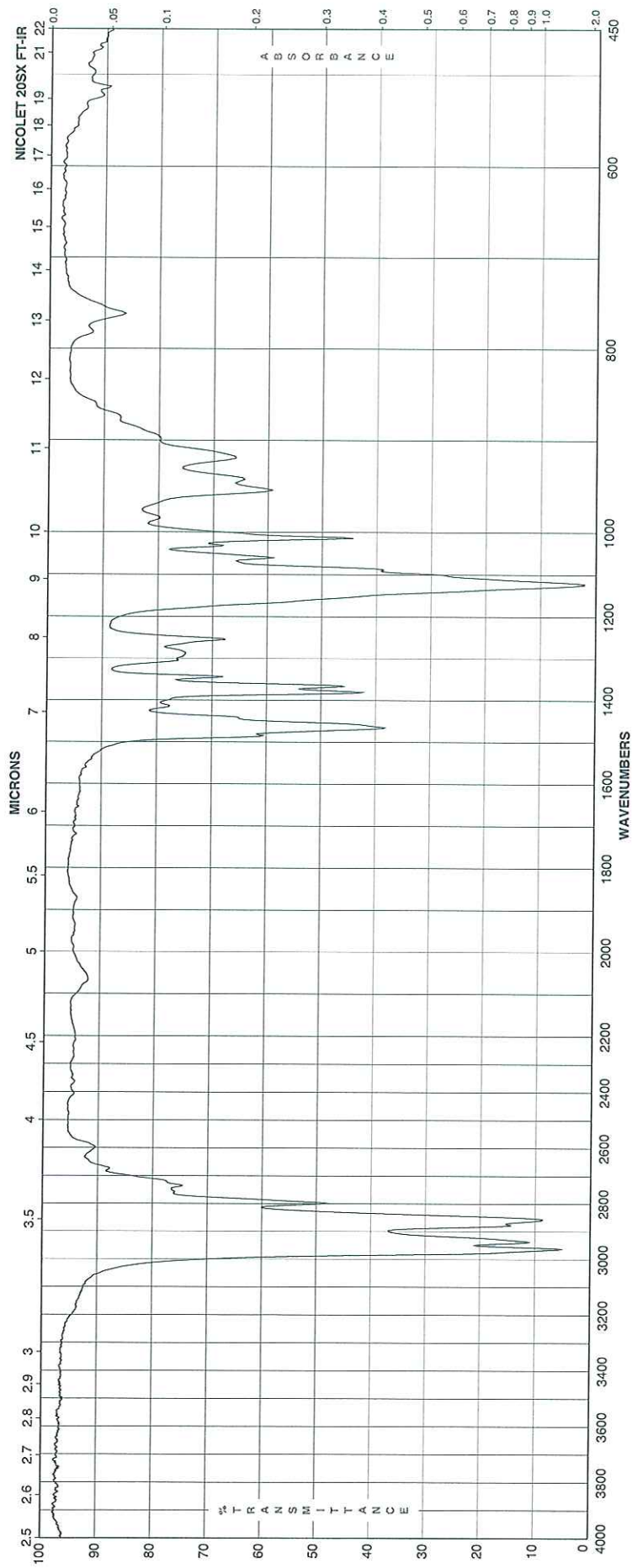


^{13}C
NMR





IR:



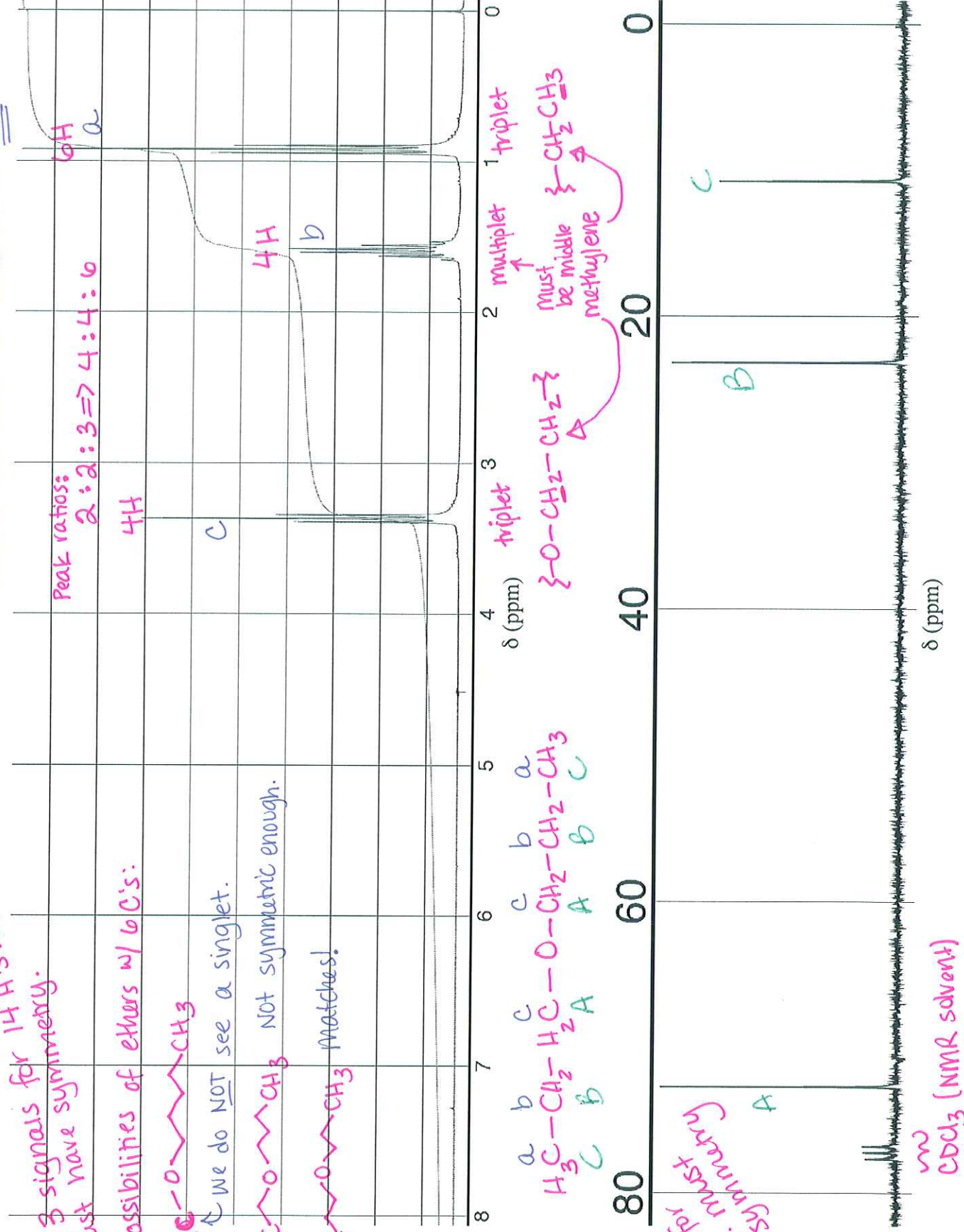
What is this unknown?



Degrees of unsaturation: $H_{calc} \Rightarrow C_6H_{14}$. If alkane, C_6H_{14} ($C_n H_{2n+2}$).
 So no degrees of unsaturation/no π -bonds or rings.
 ∴ Must be ether or alcohol... IR.

only 3 signals for 14 H's... must have symmetry.

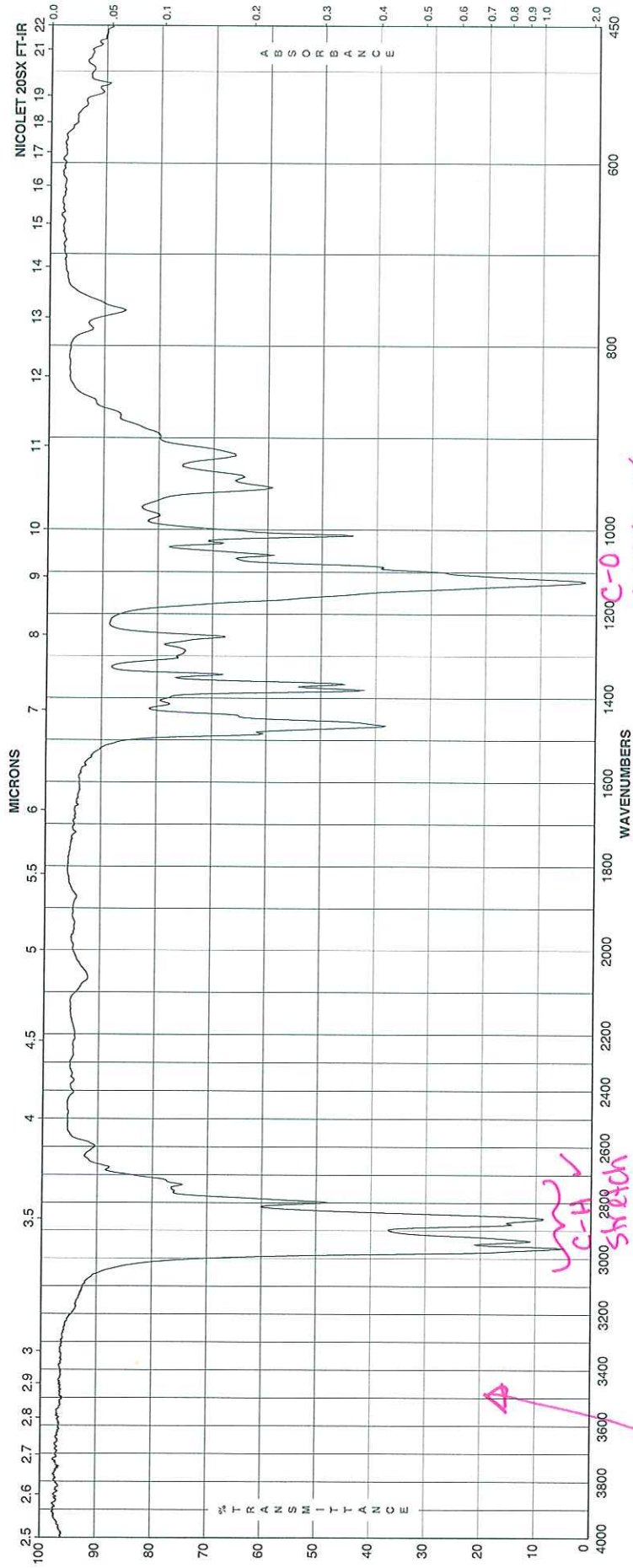
Possibilities of ethers w/ 6 C's:



only 3 signals for 6 C's... must have symmetry



IR:

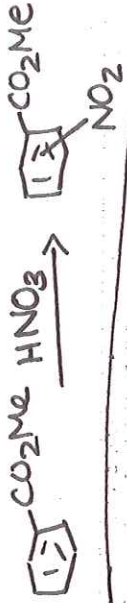


NO O-H ⇒ must be an ether.
so not an alcohol!

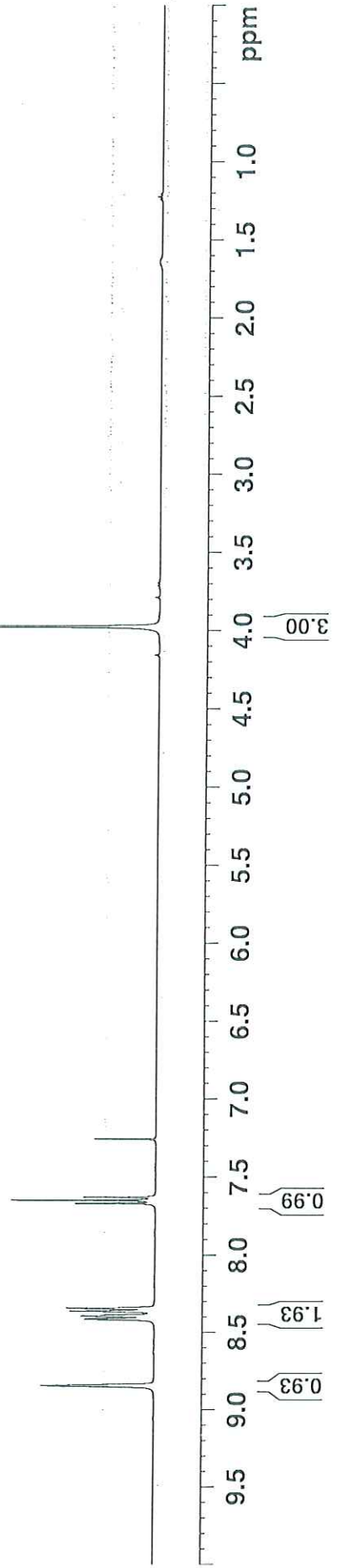
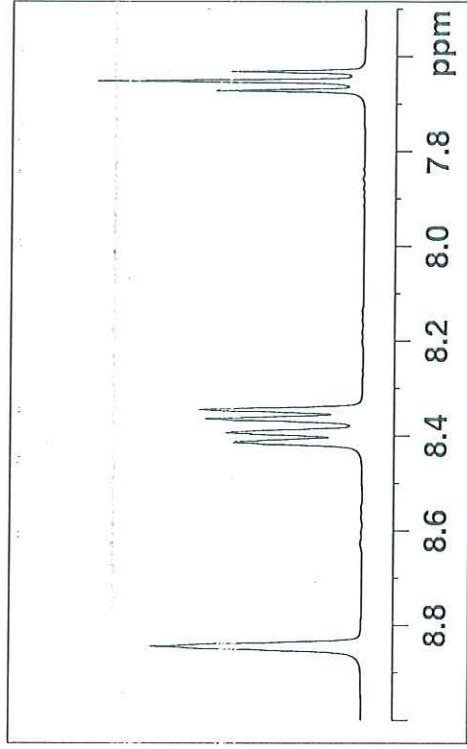
CHEM 322 - Amber's Section 36
PROTON_16 CDCl3 /opt/topspin mpwatson 6

8.43
8.415
8.412
8.396
8.394
8.392
8.364
8.345
7.671
7.651
7.631
7.261

Acknowledgements
Amber Gietter
Maddy Sambalino
Kim Meyer
Section 36 (Fri 9am)

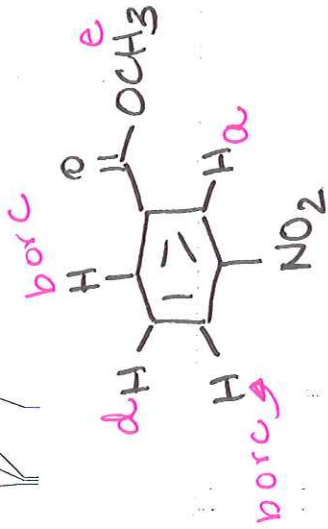
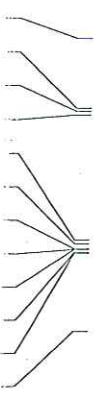


What is the regiochemistry of the product?
ortho, meta or para?

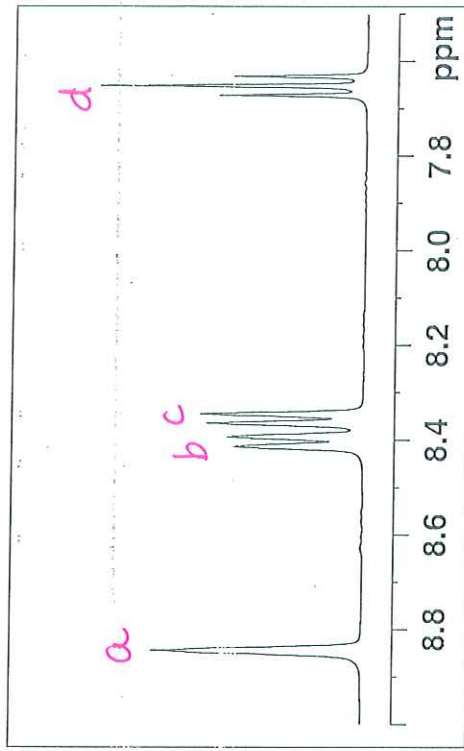


CHEM 322 - Amber's Section 36
 PROTON_16 CDCl3 /opt/topspin mpwatson 6

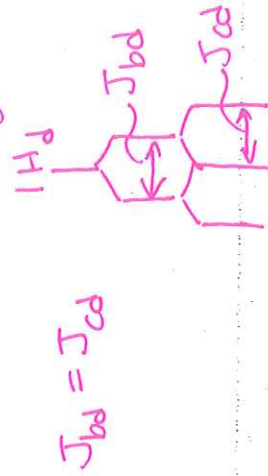
7.261
 7.031
 7.051
 7.071
 7.045
 7.364
 7.392
 7.394
 7.396
 7.412
 7.415
 7.843



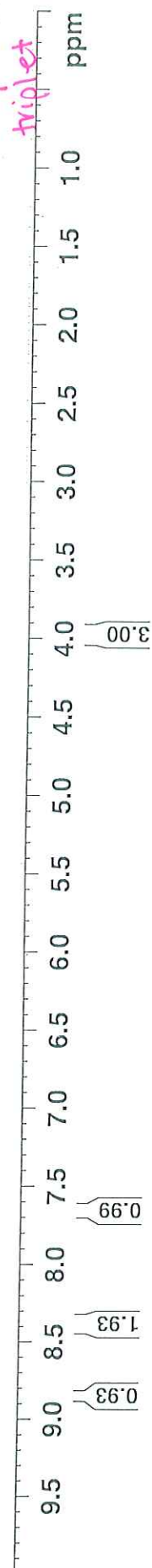
acknowledgements
 Amber Eletter
 Maddy Sambalino
 Kim Meyer
 Section 36 (Fri 9am)



Tree Diagram:



1H (singlet) → a
 1H (doublet) → b
 1H (doublet) → c
 1H (triplet) → d
 CHCl3

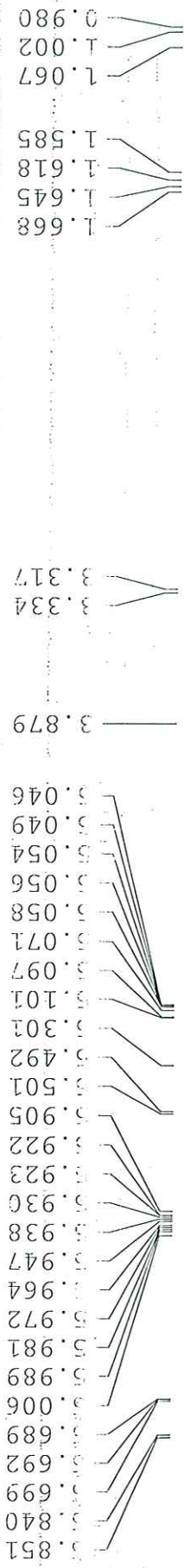


CHEM 322 - Neo's Section 26
 PROTON_16 CDCl3 /opt/topspin mpwatson 3

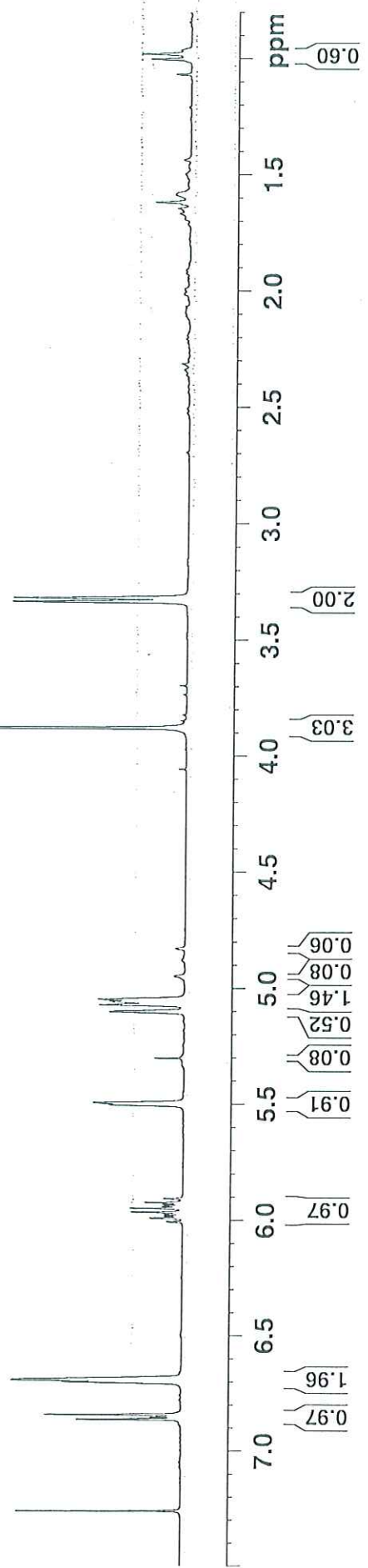
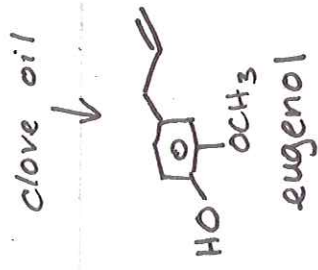
Acknowledgements

Neo Hu
 Cirrus Foroughi
 Erica Goldenberg

Noelle Tuttle
 Nikhil Patel
 Section 26 (Tues 12:30)

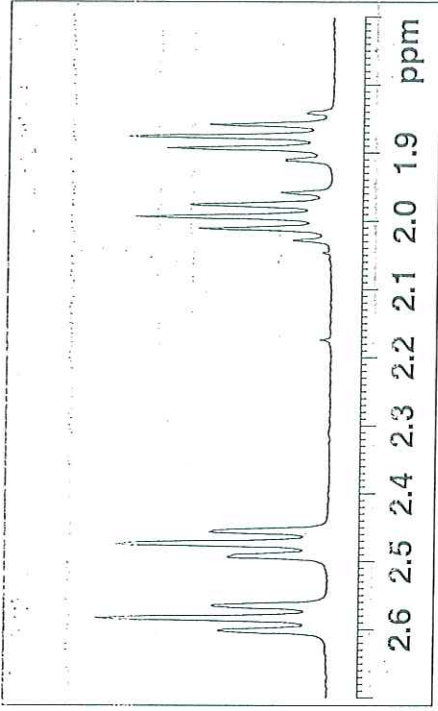
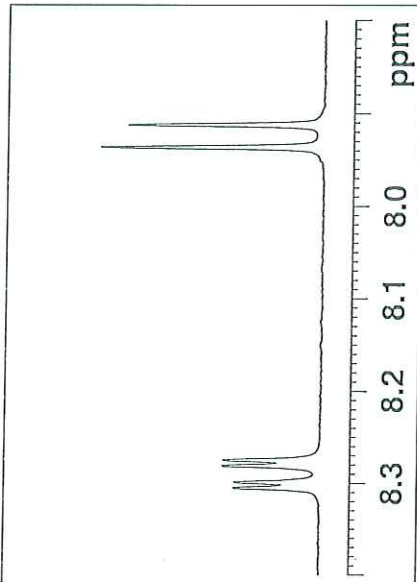
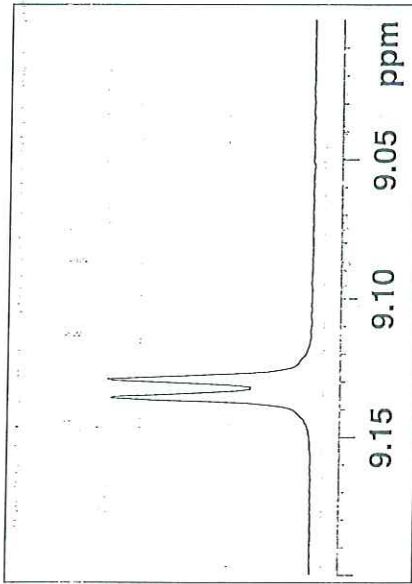


Assign peaks to compound...

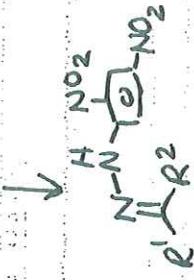


CHEM 322 - Peter's Section
 Unknown 4 Derivative
 PROTON_16 CDCl3 /opt/topspin.mpwatson 4

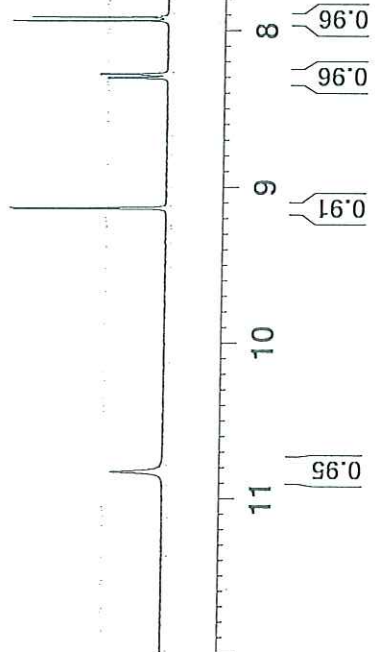
Acknowledgements
 Peter Gildner
 Matt Vahabi
 Marissa Yarnall
 Section 033 (Tues 7-10)



Which unknown did
 this group have?



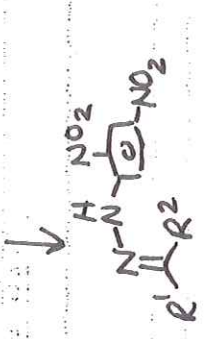
Possible
 unknowns:



CHEM 322 - Peter's Section
 Unknown 4 Derivative
 PROTON_16 CDCl3 / opt/topspin mpwatson 4

Acknowledgements
 Peter Gildner
 Matt Vahabi
 Marissa Yarnall
 Section 043 (Tues 7-10)

R^1-IL-R^2
 unknown



Possible unknowns:

